An NMR Investigation of the Effects of Different Drying Methods on Coal Structure.

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INTRODUCTION

One area for improvement in the economics of coal liquefaction is coal drying. This is particularly true for subbituminous coal and lignites of which the US reserves are huge. These coals contain significant amounts of water so that simply drying these materials before transportation to their final destination can represent a sizable reduction in cost. There is considerable evidence to show that drying has a detrimental effect on the liquefaction behavior of coals (1,2,3). As coals have both a physical and chemical structure, it is conceivable that drying affects one, the other, or both of these structures.

There do not appear to have been any systematic studies of different methods of coal drying on coal structure, and the role that water plays in enhancing, or lessening coal reactivity toward liquefaction. The overall objectives of this work are to investigate the effects of different drying methods on the liquefaction behavior of coal. Different methods for coal drying are being investigated to determine if drying can be accomplished without destroying coal reactivity toward liquefaction, thereby making coal drying a relatively economical and efficient method for coal pretreatment. Coal drying methods include conventional thermal and microwave drying at elevated temperatures, and chemical drying at low temperature. Solid-state nuclear magnetic resonance (NMR) techniques of cross polarization with magic-angle spinning (CP/MAS) are employed to measure changes in coal structure brought about by the different methods of drying and by low temperature oxidation. The initial work on the project has focused on development of standardized procedures for thermal, microwave, and chemical methods of coal drying. Results of this aspect of the project are reported in this paper.

EXPERIMENTAL

Coal Preparation

In order to study the effects of different methods for drying coal on moisture removal, a master batch sample (~500 g) of Eagle Butte subbituminous coal from the Powder River Basin, Wyoming was prepared by grinding and screening to -20, +100 mesh particle size. This sample was placed in a wide mouth jar and allowed to equilibrate in an oven with a beaker of water at 40°C for 24 hrs. The sample was then removed from the oven and placed in a humidifier until aliquots were taken for the different drying tests. The moisture values for all the coal drying tests were determined from the weight loss at 105°C for 24 hrs. The

moisture values for 2-gram aliquots from the master batch of Eagle Butte coal were 18-20% using this method.

Thermal Drying

Samples of the Eagle Butte subbituminous coal were heated to different final temperatures in order to determine at what temperature, significant structural changes begin to occur that might affect the liquefaction behavior. These heating experiments are referred to as ballistic heating experiments. The ballistic heating experiments were performed with a small, vertically aligned furnace. The furnace has a 12-centimeter long heated section which accepts a 1.4-centimeter i.d. quartz liner. A stainless steel screen provides support for the coal and a steel wool pack heats the nitrogen sweep gas which is introduced at the bottom of the quartz liner. In a typical experiment, the furnace is preheated to about 10°C above the desired final coal temperature. A 2-gram coal sample is then poured into the quartz liner and a thermocouple is inserted into the coal sample bed. When this thermocouple reaches the desired temperature, the quartz liner is removed from the furnace and allowed to cool. Nitrogen flow is maintained at all times. When the sample temperature is below 50°C the coal is poured into a sample vial, capped with nitrogen, and sealed. Heatup times with this system are typically from 15 to 20 minutes.

Microwave Drying

A number of microwave drying experiments were conducted using Eagle Butte subbituminous coal. The experiments were conducted using a CEM model MDS 81-D laboratory microwave oven that is equipped with facilities to introduce different gaseous environments, or using a commercially available microwave oven. Microwave drying tests were conducting in the following manner: ~ 2 grams of coal were placed in 25 mL beakers, and the beakers placed at the center of the microwave oven. Samples were exposed to microwave radiation for different periods of time and at different power levels, after which the samples were removed from the oven and a thermocouple inserted into the coal bed to determine an average temperature.

Chemical Drying

Chemical drying experiments were conducted on the Eagle Butte subbituminous coal, and also a Usibelli subbituminous coal from Alaska using 2,2-dimethoxypropane as a drying agent. One-half gram of coal was weighed into a 10 mL centrifuge tube followed by 2 mL of 0.2 N CH_3SO_3H in CH_3OH and 1 mL of the reference standard cycloheptane. Four mL of dimethoxypropane were then added to the mixture. The total mixture was stirred, then centrifuged for 10 minutes. After 2, 4, 6, and 8 hours, one-half mL aliquots were removed, diluted with one-half mL $CDCl_3$, and the ^1H NMR spectrum recorded. The solution was stirred and centrifuged prior to removing the aliquots.

A ^1H NMR method was developed to rapidly measure the amount of water in coal. The ^1H NMR spectra of the reaction products, methanol and acetone, give single resonances for the methyl groups, which are easily identified. These resonances do not overlap the hydrogen NMR resonances of DMP. Integration of the methyl resonances from acetone is used to measure directly the moles of water reacted. The average relative error using the ^1H NMR method is < 3% for standard solutions with a known amount of water. A curve-fitting routine

for determining the area of the peaks increases the precision and accuracy of the NMR method by eliminating instrumental and other artifacts which contribute to the peak shape.

RESULTS AND DISCUSSION

Thermal Drying

Samples of the Eagle Butte coal were ballistically heated to final temperatures of 100, 150, 200, and 250 °C. Solid-state ^{13}C NMR measurements were made on the heated samples, and are shown in Figure 1 for the starting coal, and coal heated to 150, and 250 °C. The spectra indicate that under this method of heating, there are no significant changes in carbon functionality up to temperatures of 250 °C, except for some deterioration in resolution of branched aromatic carbons (~140 ppm), phenolic carbons (~155 ppm), and carboxyl carbons (~180 ppm).

Microwave Drying

Microwave drying is an alternative thermal method of drying coals. However, the mechanism of drying with microwaves is different from that of simply heating the coal. In order for a substance to absorb microwaves and become heated, it must have a permanent dipole moment. Therefore, the functional groups that are the most efficient absorbers of microwaves are those that are highly polar, such as the -OH group in water.

When a substance containing water molecules is exposed to microwaves of the proper frequency (2,450 MHz) the water molecules attempt to align and realign with the alternating electric field of the microwaves. This causes friction at the molecular level, which becomes manifested as heat. Because the water in coals can be distributed on the surface, in pores, or as part of the coal structure as in a gel, depending on rank, microwaves might be used to provide some selectivity for coal drying without appreciably affecting the overall coal structure and liquefaction behavior of the coal.

The objective of the microwave drying subtask is to determine whether microwave drying alters the structure and composition of the coal, and hence its behavior toward liquefaction. This work was prompted by earlier work of Silver and Frazee (1) that showed that drying coal with microwaves beyond ~75% moisture removal actually had a detrimental effect on the reactivity toward liquefaction. However, there has not been a systematic study of changes in coal structure induced by microwave drying.

At full power (600 watts), 75 % or greater of the moisture was removed in ~2 min., and removal of the remaining moisture caused the temperatures to increase rapidly (Figure 2). Because of the rapid moisture removal at full power, different levels of microwave power were used in order to obtain a more complete drying curve. At power levels of 300 watts, 25 -75 % moisture could be removed for irradiation times of up to 15 min.

The general features of the coal drying curves using microwave radiation are shown in Figure 2. In general, there is a very rapid temperature rise after ~10 % of the moisture is removed. This is followed by removal of the bulk of the moisture (10-80%) at temperatures close to the

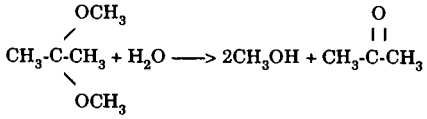
boiling point of water, which is ~ 93°C at the 7,200 ft elevation in Laramie, WY. The rapid increase in temperature after >75% of the moisture is removed seems to be a general characteristic of microwave heating of subbituminous coals. This behavior was also observed by Silver and Frazee (1), who also noted a decreased reactivity toward liquefaction for greater than 75% moisture removal. We speculate that beyond this level of moisture removal, the additional moisture that is removed is an integral part of the gel or pore structure of the coal. These water molecules have a more difficult time aligning and realigning with the radiation field, and thus would cause heating to higher temperature, and possible disruption of part of the coal matrix enabling some retrograde reactions to take place that diminish the reactivity toward liquefaction.

It was possible to remove greater amounts of moisture than that determined by thermal drying, by microwave drying for extended periods of time (180 min) using lower power levels (300 watts). These results are shown in Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of the microwave heated coals are shown in Figure 4. The spectra do not show any significant carbon structural changes as a result of moisture removal using microwaves, even though the temperatures were greater than 100 °C and greater than 100% of the moisture removable by thermal drying at 105°C was removed using microwaves. In general, there is a slight degradation in the resolution of some of the carbon functionality during heating, as evidenced by the smoothing of the resonance bands at ~140, 155, 180 ppm, similar to what was observed in the ballistically heated samples (Figure 1).

Chemical Drying

Chemical drying of coals is a relatively unexplored technique for removing water at low temperature. Thermal methods of drying can alter the physical structure of coal as well as promote undesirable chemical reactions. Low-temperature drying of coal, on the other hand, should preserve the structural integrity, reduce retrograde reactions, reduce thermal degradation, and provide information on nonbonded, chemisorbed, and physisorbed water. This method of dehydrating coal should provide a baseline for studying initial stages of retrograde/condensation reactions. That is, decarboxylation and low-temperature oxidation reactions can then be studied in the presence and absence of water and gases and as a function of temperature.

Pore water and surface adsorbed water on coal can be effectively removed by the use of chemical dehydration agents which react with water to form volatile reaction products. We are investigating the use of a unique chemical dehydrating agent, 2,2-dimethoxypropane (DMP), for chemically drying coals. The reaction of DMP with water is as follows:



This reaction is rapid (<10 min) and endothermic. The use of DMP to dehydrate coal accomplishes two things: (1) the removal of water at ambient temperature by chemical means rather than by physically forcing exchange by mass action preserves the structural integrity

of the coal components and (2) the reaction products can easily be measured quantitatively to determine the amount of water in coal.

The results of the chemical drying experiments are summarized in Figure 5. As expected, the measured moisture content increased with time and reached a maximum after about 8 hrs. The data suggest that two types of water are removed sequentially. Free or surface sorbed water is rapidly removed upon contact with the drying agent, followed by removal of more tightly bound water as the reagents diffuse into the micropore structure. There appears to be an induction period of about 4 hrs for the Eagle Butte coal before the moisture content increases more rapidly due to removal of the more tightly bound water.

The chemical drying experiment was repeated twice for the Usibelli subbituminous coal. In the first experiment, aliquots were removed sequentially, and in the second experiment, separate coal samples were prepared and allowed to stand until the appropriate time for acquisition of the ^{1}H NMR spectrum. The data show excellent reproducibility.

Both coals were thermally dried at 110°C for 1 hour. The moisture content was determined by weight loss. Eagle Butte coal had an as determined moisture content of 16.6 wt% and the Usibelli had an as determined moisture content of 14.1 wt%. These values are close to the early time moisture contents determined by chemical drying.

ACKNOWLEDGMENT

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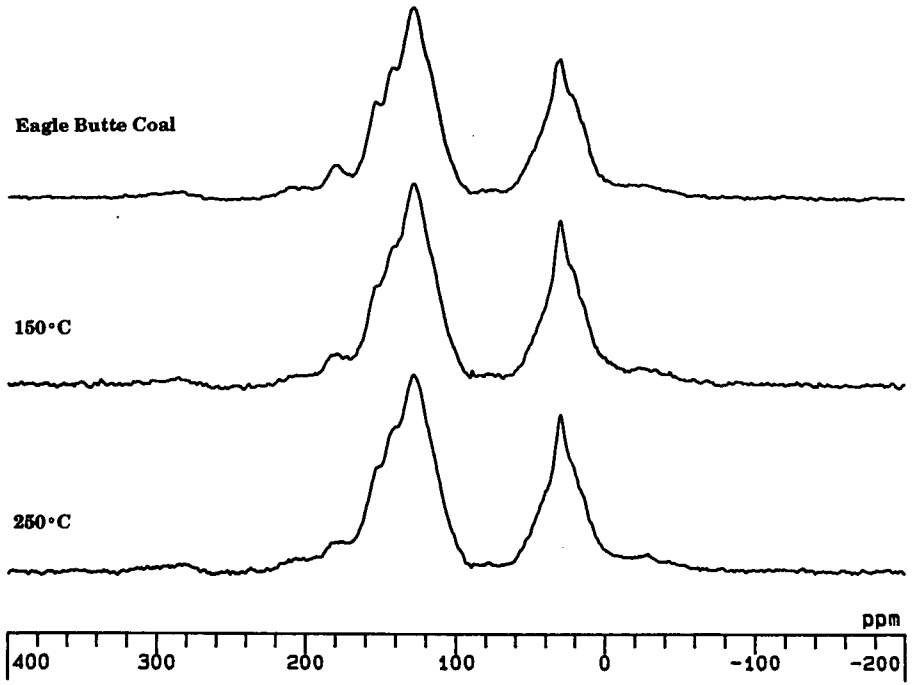

Figure 1. CP/MAS ^{13}C NMR spectra of ballistically-heated Eagle Butte subbituminous coal.

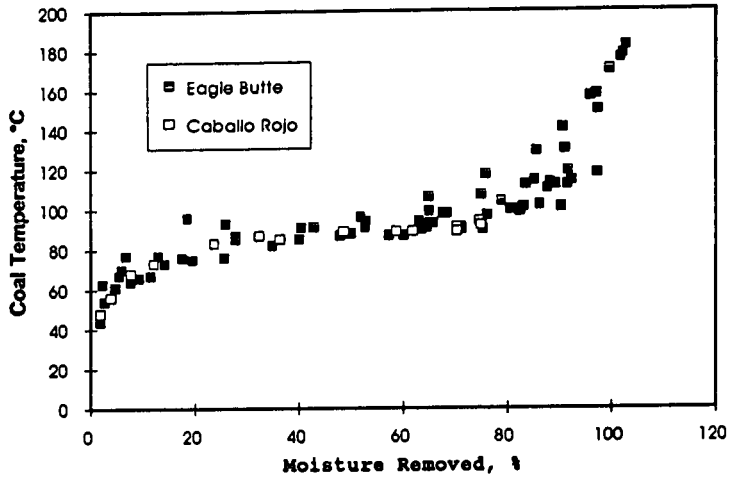

Figure 2. **Coal temperature as a function of moisture removal for microwave drying.**

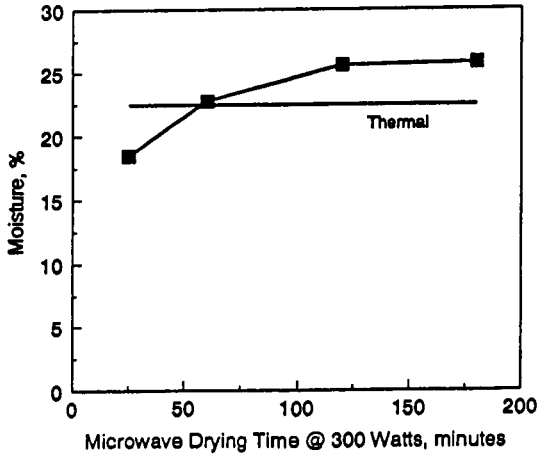

Figure 3. Moisture removal as a function of microwave drying time at 300 watts.

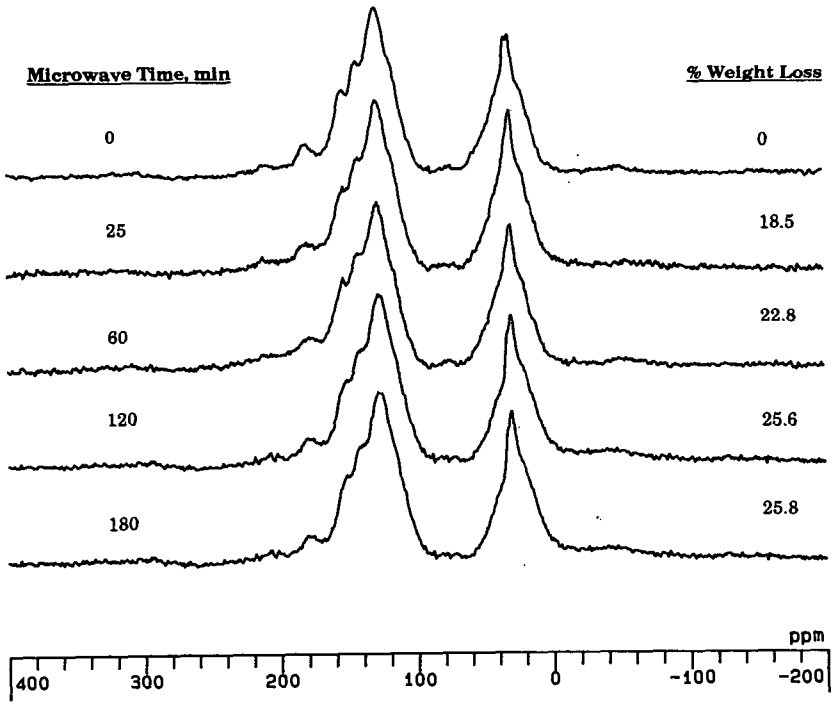

Figure 4. CP/MAS ^{13}C NMR spectra of microwave-dried Eagle Butte coal (weight loss from thermal drying = 22.5%).

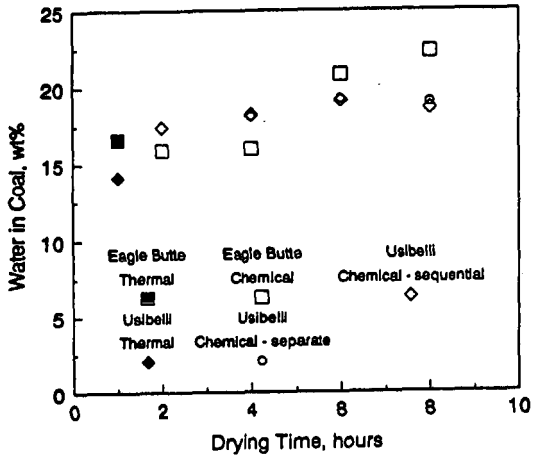

Figure 5. Moisture removal as a function of time for chemical drying.